

The influence of batch processing on the particulate properties of burkeite ($\text{Na}_2\text{CO}_3(\text{Na}_2\text{SO}_4)_2$)

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Studies of the particle porosity as a function of residence time associated with the crystallization of high surface area burkeite ($\text{Na}_2\text{CO}_3(\text{Na}_2\text{SO}_4)_2$) agglomerates revealed no evidence for Ostwald ripening. However, a significant increase in particle porosity was observed following milling, reflecting particle breakdown and the consequent exposure of more particle surface to the liquid phase. The action of spray drying was found to reverse this trend with the particulates so formed exhibiting a much lower porosity, reflecting the blocking of surface pores by recrystallized material.

1. Introduction

Carbonate- and sulphate-based materials can be crystallized to form high surface area, highly porous powders, which can be used for a variety of purposes. One usage of particular interest of these materials is as carrier materials as well as builders in the detergent industry. A carrier material is composed of a crystalline matrix which forms a porous, close-packed structure. Pore size is typically of the order 0.1–50 μm . However, a pore-size range of 0.5–3 μm is normally desirable for detergent operation, allowing efficient uptake and retention of the various liquid components required for washing duty, e.g. surfactants, perfumes, etc. For maximum liquid-carrying capacity, a carrier requires a high internal porosity and a pore size that is significantly smaller than the inter-particle pore-size distribution. The optimum method of achieving this is to have the crystallization and agglomeration of dendrites, forming a matrix.

Common detergent builders are phosphates and carbonates. Sodium tripolyphosphate hexahydrate $\text{Na}_3\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ was the dominant carrier for many years due to its ease of formation and ready modification to the optimum dendritic form, as well as being a very effective builder. However, environmental considerations (e.g. eutrophication of lakes, etc.) have lead to a search for alternative materials that can be utilized as builders. Sodium carbonate monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and the double salt, burkeite Na_2CO_3

(Na_2SO_4)₂ can be, and have been, employed as replacement builders/carriers for phosphates, principally because carbonate- and sulphate-based materials are relatively inexpensive, easy to obtain and are ecologically acceptable [1–3]. Both burkeite and sodium carbonate monohydrate were first considered unsuitable as detergent builders/carriers owing to their tendency to form “block-like” agglomerates, with a pore-size distribution too large for effective uptake and retention of the various detergent components. However, certain polyacrylates allowed both burkeite and sodium carbonate monohydrate to be habit modified sufficiently to be used as effective carriers with the adequate pore-size distribution for maximum uptake of the various liquid components [4]. The optimum porosity has been previously determined for a burkeite builder to occur within the pore size range 0.5–3 μm .

Previous work has concluded that the degree of agglomeration decreases with increasing intensity of agitation, mean crystal size and solid concentration [5] and increases with supersaturation [6, 7] to a maximum plateau. Agglomeration can be separated into two areas:

(a) where the agglomeration occurs in the sub-micrometre range with no well-developed crystals [5, 8, 9];

(b) where well-developed single crystals occur which then agglomerate over a large size range [5, 10].

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In most crystallizing systems, the rate of crystallization is high, leading to small particles within the system. This will maximize the agglomeration [8, 9], leading to the former case. The latter case is rarer and usually occurs at low supersaturations. The burkeite systems under consideration have been assumed as being examples of the former case. Different mechanisms have been proposed for agglomeration depending on whether the agglomeration is induced by fluid-mechanical processes, e.g. orthokinetic agglomeration, or whether agglomeration is due to particles subjected to collisions during Brownian motion, e.g. perikinetic agglomeration [11]. The effects on agglomeration and crystallization by choice of impeller have not been thoroughly investigated. Agglomerate breakdown can occur by various processes – collisions between the impeller or vessel walls and the agglomerates, collisions between the agglomerates themselves, or agglomerate breakdown due to stresses induced by fluid motion. There has been controversy over the mechanism of agglomerate breakdown: Shamlou's model [12] proposed the erosion of agglomerates due to fluid-induced stresses, rather than the total fragmentation model that has been proposed by DeBoer and others [13]. The evidence for agglomerate breakdown due to collisions between the agglomerates themselves is rather contradictory and requires further investigation.

In the present work we studied the crystallization and agglomeration of habit modified burkeite and the resultant conversion to a powder suitable for detergent operation. In particular, an understanding was sought of whether the optimum pore-size range occurred during the initial crystallization/agglomeration period or during spray drying. Within a saturated slurry, there is a tendency for small particles to dissolve and larger particles to grow larger (Ostwald ripening), to minimize the surface energy of the system [14]. Hence, the slurry will tend towards a monosize particle-size distribution. The possibility of this phenomenon existing for burkeite, thus influencing the particle agglomeration/powder porosity was investigated.

2. Experimental procedure

A slurry comprising 23.42 kg H₂O, 1.66 kg sodium polyacrylate, 13.48 kg sodium sulphate, 5.17 kg sodium carbonate, 1.05 kg alkali silicate and 0.22 kg alcohol ethoxylate was prepared at 85 °C in a 100 lb batch crystallizer. The slurry was agitated using a multi-stage pitched-blade impeller, with an impeller/vessel diameter ratio of 0.82. Crystallization was initiated by the addition of the carbonate component. Samples were then withdrawn from the crystallizer, washed and stored in *n*-hexane after the following residence time intervals: 5, 15, 30, 60, 120 and 240 min. After this the slurry was milled twice and spray dried. The conditions for the latter were tower diameter 1.8 m, air inlet temperature 350 °C, air flow rate 50 kg/min⁻¹, spray nozzle diameter ratio (inlet/outlet) 2.54 mm/1.78 mm. The powder samples from the slurry were filtered and the solids dried for 12 h at 80 °C.

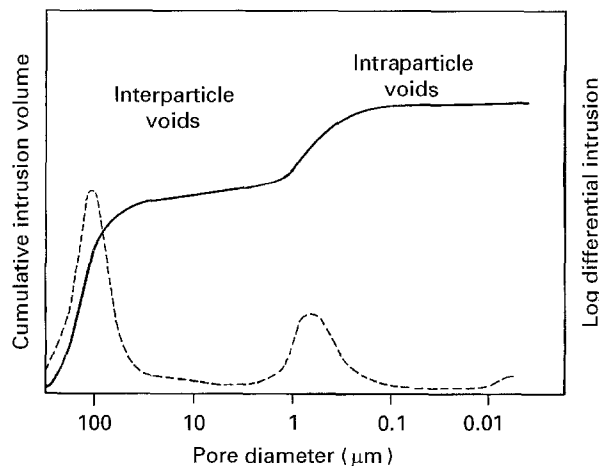


Figure 1 Schematic graph showing the relationship between mercury uptake and the pore size of the particulate material.

The resultant particulate solids were analysed using X-ray powder diffraction to identify the dominant phases present, scanning electron microscopy (SEM) to deduce particle morphology, and energy dispersive microanalysis to cross-correlate phase with particle morphology. The particle porosity was measured using mercury intrusion porosimetry from which the pore-size distribution can be split into regions of interparticle and intraparticle pore volume distributions (Fig. 1). The former region is where the measured porosity is attributed to pores between particulates (normally 70–100 μm), whereas the latter is a measure of a particle's internal porosity. Previous studies had assumed that the region between 0.5 and 7 μm was the region of internal porosity that exhibited good uptake of post-dosed liquids. However, this does not show good correlation with studies of powder uptake capacity. A reassessment showed that in general, the region 0.5–3 μm is the region of intraparticle porosity for burkeite that exhibits good correlation with studies of powder uptake capacity; a typical uptake capacity range for a standard spray-dried burkeite powder being 0.4–0.6 ml g⁻¹. This figure is significantly reduced by the presence of certain anions, e.g. Ca²⁺ and to a lesser extent Mg²⁺ in a burkeite slurry. These anions lead to a reduction of the intraparticle pores of optimum liquid uptake by modifying the crystal growth and resultant crystal morphology. There is also evidence that mixing and spray-drying conditions (e.g. nozzle pressure) can influence porosity.

3. Results and discussion

3.1. Particle development during crystallization

The development of burkeite as a function of time can be observed using powder diffraction (Table I). It was found that burkeite tends to form rapidly after the addition of sodium carbonate, as can be seen from the data of the sample taken after 5 min residence time: equal proportions of burkeite and sodium sulphate are observed. The proportion of burkeite gradually increases until complete burkeite formation is observed between 60 and 120 min residence time. Fig. 2 shows scanning electron micrographs which reveal the

development from large (250–300 μm) low-porosity particulates, through to the formation of smaller, more porous particles of burkeite. The small pores appear to be formed by an “edge to face” mechanism by which the plate-like burkeite crystals agglomerate (Fig. 2e–g). The results from the porosity measurements taken from the slurry samples are given in Fig. 3 and Table I. It can be seen that throughout the pore sized investigated there is little difference in porosity between the slurry samples taken after 120 and 240 min residence time; Fig. 2e and f confirm this observation. If Ostwald ripening was occurring, then growth of the larger particles would continue, whilst the smaller particles would dissolve. These changes

would obviously influence to pore-size distribution. However, over a 120 min period (between 120 and 240 min residence time) there was no apparent changes in the measured porosity in the pore size investigated; implying that there was no change in the pore-size distribution. Hence, it may be concluded that no evidence for Ostwald ripening was found for burkeite crystallization. The changeover to complete burkeite formation is also apparent throughout the pore-size range investigated, i.e. within the inter- and intra-porosity range, the cumulative volume is higher throughout for samples taken after 120 and 240 min residence time, compared to samples taken after 5, 15, 30 and 60 min residence time.

TABLE I. Analysis of phase composition and its correlation powder porosity as a function of residence time. A, Sodium carbonate, B, burkeite

Residence time (min)	Phases formed	Inter-particle pore size (μm)	Intra-particle pore size (μm)	Total porosity (ml g^{-1})	Internal porosity (ml g^{-1})
5	A + B	90	0.5	0.68	0.11
15	A + B	85	0.4	0.92	0.19
30	A + B	103	0.3	1.03	0.18
60	A + B	103	0.38	0.98	0.18
120	B	70	0.4	1.33	0.28
240	B	90	0.4	1.19	0.30
Milled slurry	B	108	0.45	0.98	0.57
Spray-dried slurry	B	90	0.3	1.49	0.37

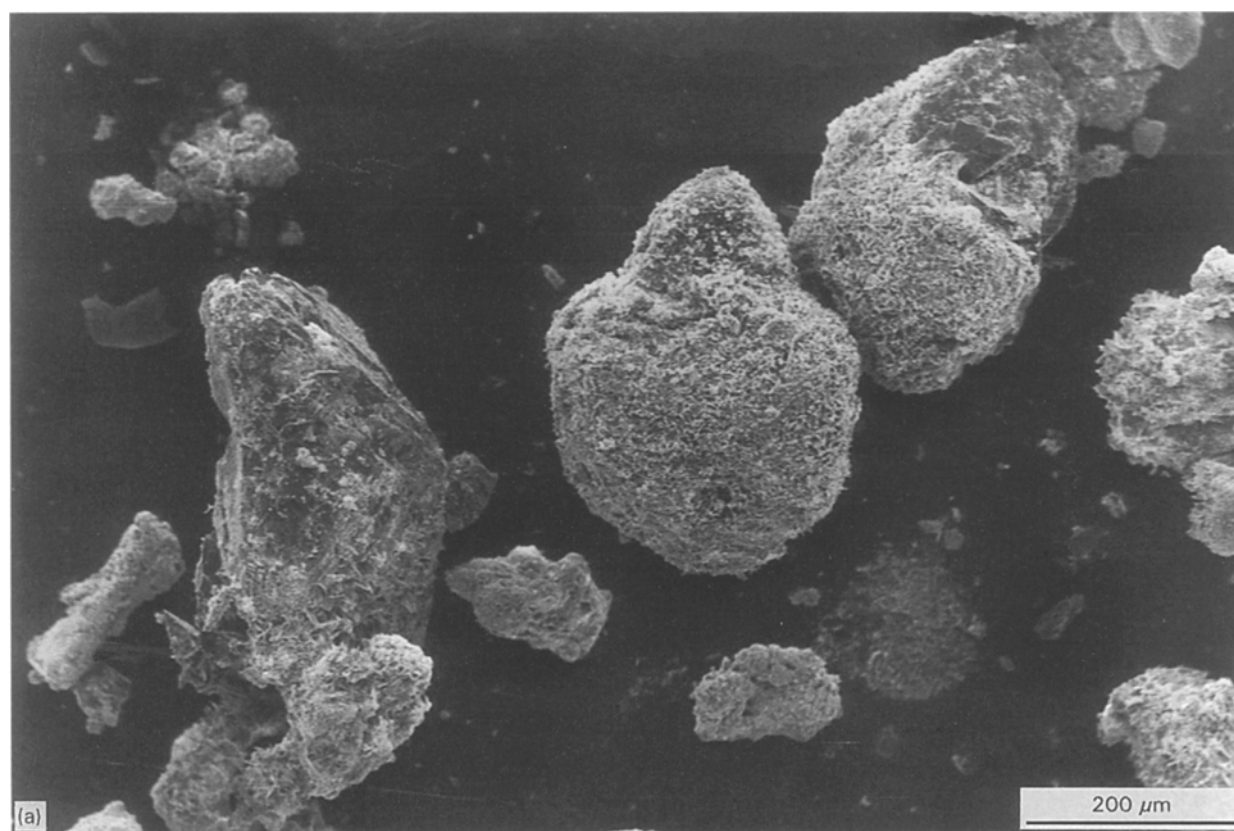


Figure 2 Scanning electron micrographs showing the development of crystallized product as a function of residence time in the crystallizer: (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min, (e) 120 min, (f) 240 min.

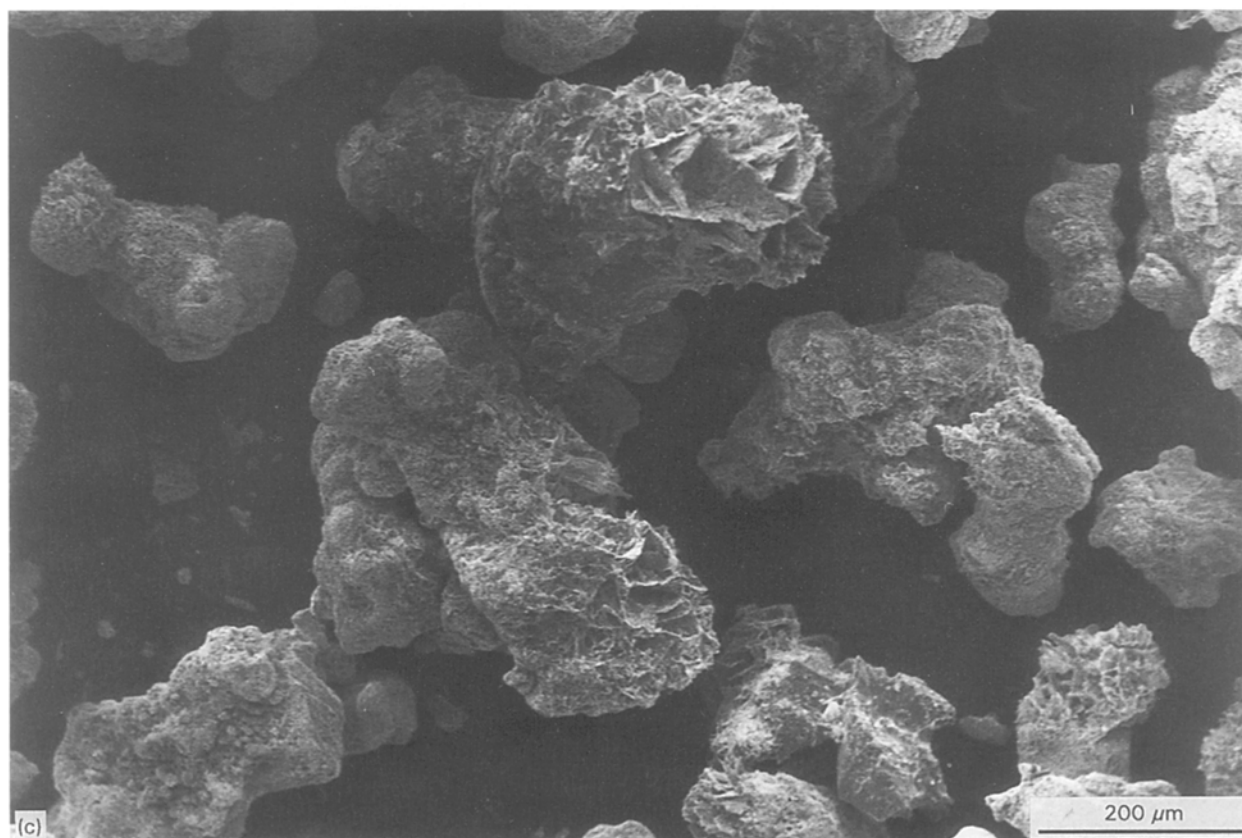
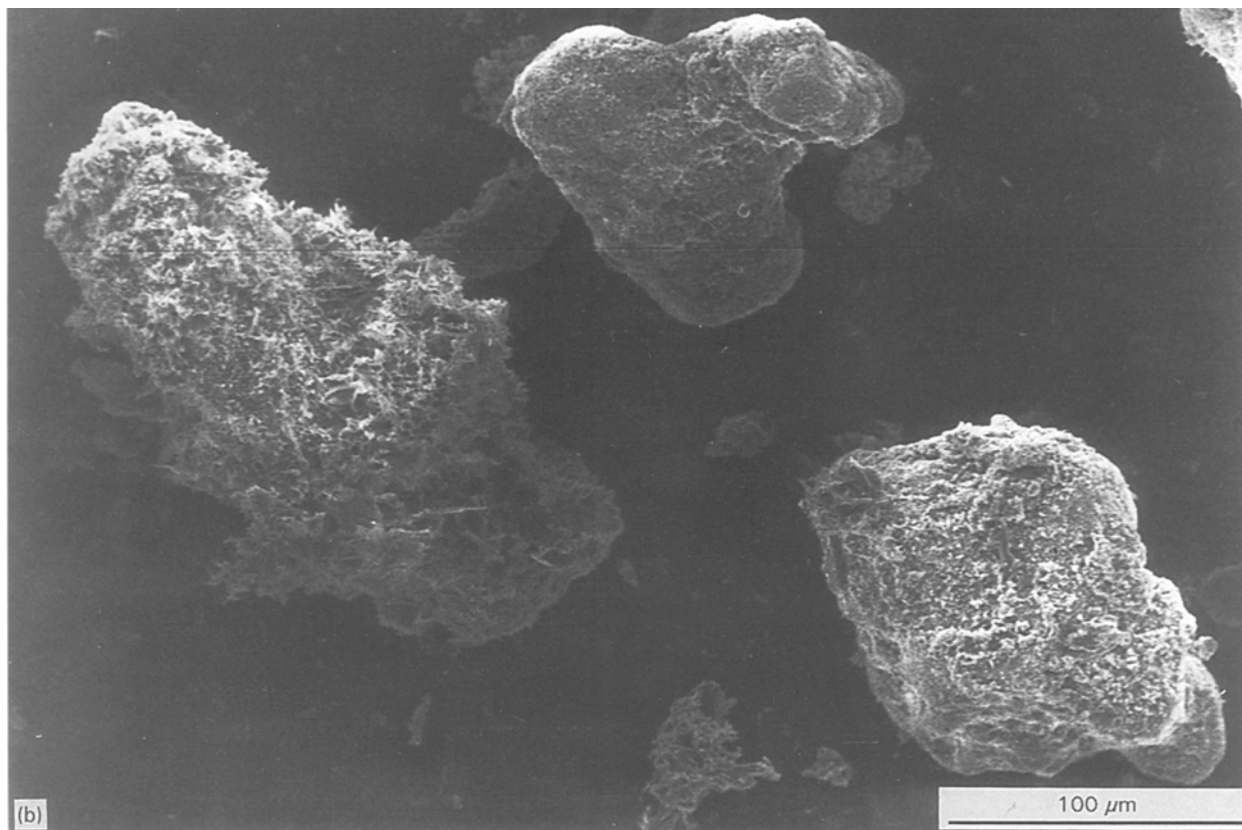


Figure 2 (continued)

3.2. Particle properties following milling and spray drying

Examination of the milled sample in the range investigated revealed the porosity to be significantly higher than that of the sample extracted during crystalliza-

tion. A possible reason for this is that the milling process breaks down large agglomerates, exposing much more of the intraparticle porosity for liquid uptake. An example of this may be seen in Fig. 4a, where the internal pores of the particles are clearly

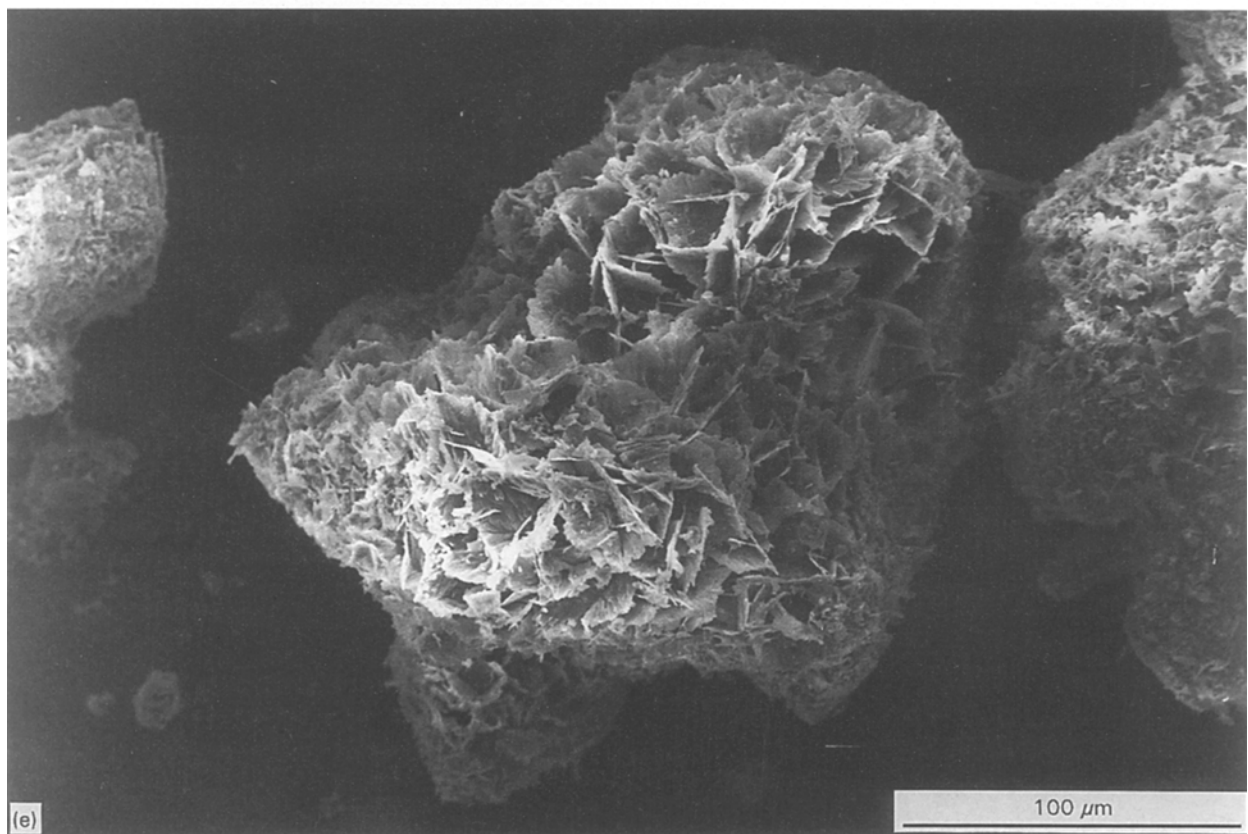
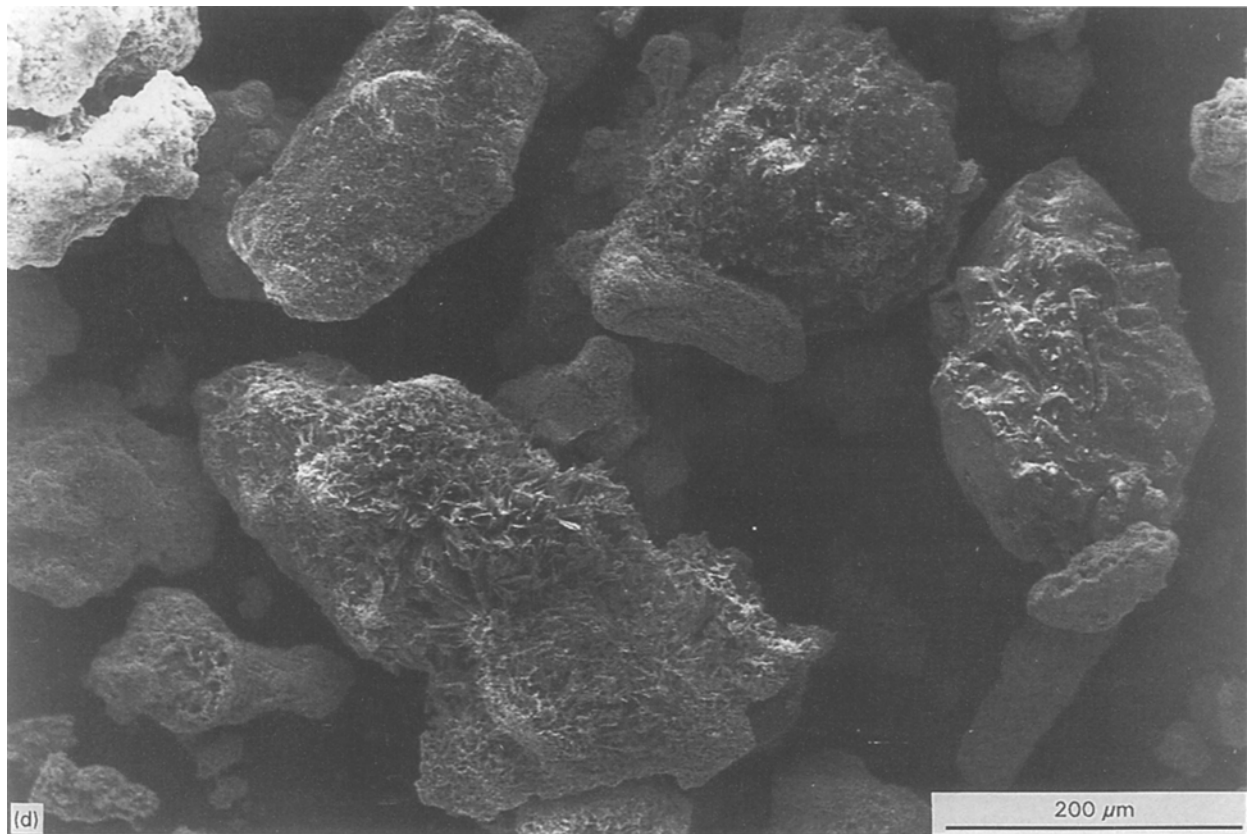


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exposed for liquid uptake. However, the porosity of the spray-dried powder is less than that of the milled sample, especially in the internal porosity range. One reason for this difference may be that when the feed enters the drying medium, the rapid evaporation

causes particles to dry, forming an outer “crust”. Large holes develop in these particles when moisture beneath the crust is removed, thus disrupting the particle packing and hence porosity/liquid uptake. Another possibility is that solution dries on the

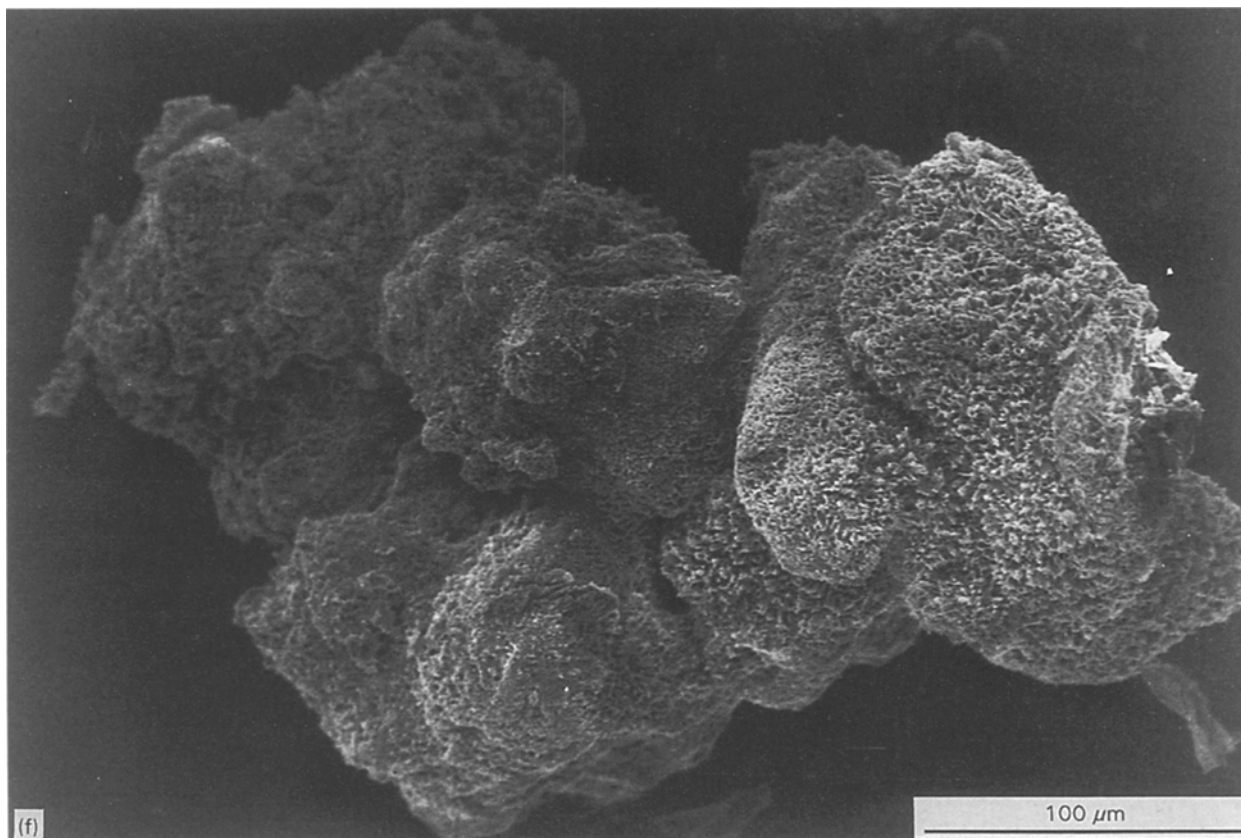


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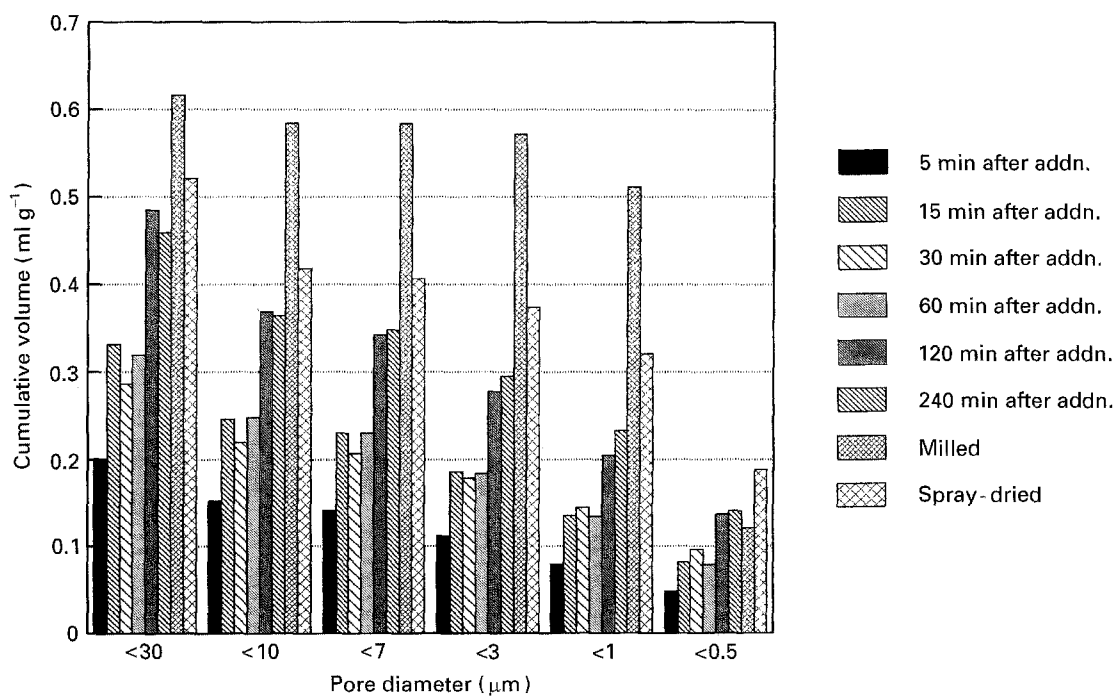


Figure 3 Histogram showing the cumulative volume versus pore-size diameter as a function of carbonate addition.

surface of the particles thus blocking pores and reducing porosity. The typical spherical particles formed by spray drying are illustrated in Fig. 4b.

A comparison between slurry and spray dried samples agitated under the same conditions can also be made from Fig. 3. Comparison of the sample taken after 240 min residence time and the

samples taken after spray drying illustrate the uptake in the optimum pore range for the slurry sample to be 0.30 ml g⁻¹ whereas for the spray-dried sample it is 0.37 ml g⁻¹. This thus confirms that a significant proportion (81%) of the desired porosity occurs during the initial crystallization/mixing stages.

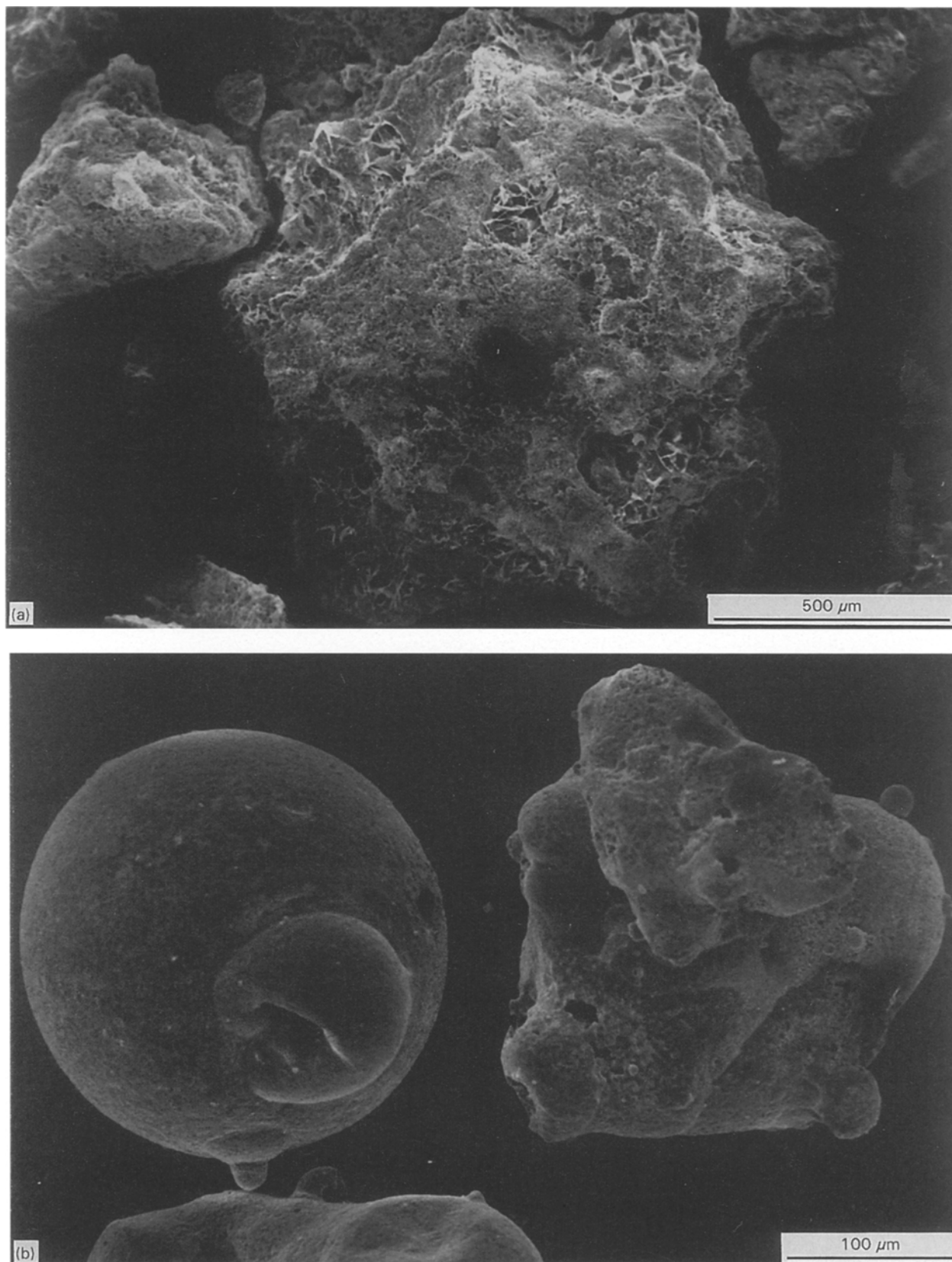


Figure 4 Scanning electron micrographs showing the particle morphology following crystallization: (a) after milling, (b) after spray drying.

4. Conclusion.

Residence time studies highlighted the development of burkeite as a function of time, after materials addition was completed. Shortly after final materials addition, the phases present were identified as burkeite and sodium sulphate, the percentage of burkeite present

increasing as time increased. Complete burkeite formation was observed to take place between 60 and 120 min residence time. Over a period of 120 min, no change in the pore-size distribution was observed, implying that Ostwald ripening is not a factor in the crystallization of burkeite.

From comparison of the liquid uptake of a burkeite slurry sample to a spray-dried sample prepared under the same mixing conditions, it may be seen that at least 47% and up to 70% of liquid uptake in the desirable pore region occurs during the mixing/crystallization stage. However, liquid uptake for a milled sample is much higher than the spray-dried sample, which may be attributed to either the agglomerate breakdown by the milling process, exposing a greater percentage of particle internal porosity than is present in the spray-dried sample, or possibly during the drying process solution dries on the surface of the spherical particles, thus blocking pores and reducing porosity. The rapid removal of water during spray drying, disrupting particle formation and packing, may also account for the apparent drop in porosity between the spray-dried and milled samples.

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